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**FIBER REINFORCED METAL COMPOSITES UNDER
STUDY AT LEWIS RESEARCH CENTER**

by **J. W. Weeton and R. A. Signorelli**
Lewis Research Center
Cleveland, Ohio

TECHNICAL PAPER proposed for presentation at
14th Refractory Composite Working Group Meeting
sponsored by the **U. S. Air Force Materials Laboratory**
Wright Patterson Air Force Base, Ohio, May 6-22, 1968



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D.C. • 1968

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INTRODUCTION

In past meetings of the Refractory Composites Working Group representatives of the Lewis Research Center have described their work on bulk refractory metals and coatings for superalloys and refractory metals. A large percentage of the work being done at Lewis in the Materials and Structures Division is oriented toward the ultimate use in advanced gas turbines. This is also true for the fiber composite materials research in our Division. Although in the past the composite materials work at Lewis was restricted to fiber-reinforced metal matrix material, work is being conducted today in the Structural Mechanics and Polymers Branch on fiber reinforced plastic matrices. No attempt will be made in this paper to describe this work but rather the continued efforts of the Fiber Metallurgy Section of the Composite Materials Branch will be described. The areas to be described are: Model systems, engineering materials, whisker composites, polycrystalline ceramics, and the direction of future programs.

MODEL SYSTEMS STUDIES

In recent years the strengthening mechanisms associated with fiber reinforced metallic materials have been summarized and presented in numerous articles and textbooks. The law of mixtures was first shown to represent strength relationships for metal fiber-metal matrix composites in a 1959 publication (1). This work was later expanded to include parameters other than tensile strength (2 and 3). Figure 1(a) and (b) shows the strength of tungsten fibers and a copper matrix and the fact that the composite strength varies as the volume percent of tungsten fibers increases for both continu-

ous and discontinuous fiber composites. The strength of such composites was found to be represented by

$$\sigma_c = \sigma_f A_f + \sigma_m^* A_m \quad (1)$$

where

σ ultimate tensile strength

A area fraction or volume fraction when unity length is considered and $A_f + A_m = A_c = 1$

σ_m^* stress on matrix, taken from stress-strain curve, at equivalent strain to that at which ultimate tensile strength of fiber is achieved

and the subscripts are

c composite

f fiber

m matrix

A modification of this equation to account for end effects of short length fibers has been given in (4). The equation is as follows:

$$\sigma_c = \sigma_f V_f \left(1 - \frac{L_c}{2L} \right) + \sigma_m^* (1 - V_f) \quad (2)$$

where

σ tensile strength

V_f volume fraction of fibers or same as A_f of eq. (1)

σ^* same as that for eq. (1)

$(1 - V_f)$ V_m , volume fraction of matrix or A_m of eq. (1)

L actual fiber length

L_c fiber length needed to permit fiber to contribute its tensile strength to composite, that is, critical fiber length

Other modifications to account for degradation of the fiber involve multiplying the fiber strength by a factor to account for the reduction in the strength of the fiber during fabrication. Restraint effects and possibly other synergistic effects will certainly be evident as more studies are made but the basic working calculations are based on the law of mixtures equation, as simple as it is. It is also important to know that the high temperature behavior of composites in tensile tests are very similar to those at lower temperatures, at least for the model materials selected for the Lewis studies. The next figure 2 (5) shows some high temperature tensile test data for tungsten-copper matrix composites. The ductilities of these materials (reduction in area) are shown in figure 3 for the same range of test temperatures. Note that reduction in area values are appreciable over the entire test temperature range.

In some high temperature tensile tests of discontinuous tungsten fiber reinforced copper matrix material, it became very evident that two factors; length-to-diameter ratio and fiber orientation, were very important in influencing the strength of the composites. Although chromium was used as a matrix additive in one set of composites, only the work on the copper model system will be described. Figure 4 shows the strength of composites at temperatures of 300°, 900°, and 1500° F plotted against the volume percents of the fibers in the composite (6). The upper curves represent law of mixtures strengths for composites containing continuous length fibers, from Ref. 5. Curves with the dashed lines represent strengths of composites with various length to diameter ratio fibers. It can be seen that, at the higher temperatures, as the length to diameter ratio decreases from continuous length fiber

to 200/1 or 100/1, the strength of the composites go well below the law of mixtures lines for continuous fibers. The lines drawn through the points incidentally represent calculated lines using equation (2) given previously. These figures also indicate, by the closed versus the open data points, whether the failures of the specimens were tensile or shear failures. Those data points half solid and half open represent a combination of fiber tensile failure and matrix shear. The shear failures (the solid points) are well below the calculated line. The data points representing tensile failures fall close to the calculated lines. It was observed that those materials that failed by shear contained fibers which were misoriented from the axis of the specimen by only 3-4°. Specimens that had tensile failures contained fibers aligned within 2° of the specimen axis. Figure 5 shows a blow-up of some of the details presented in figure 4 for the material with a fiber length to diameter ratio of 100 tested at 1500° F. The angle of misorientation at which a failure changes from tensile to shear, is termed the critical angle and was determined to be 3° using the following equation:

$$\phi_{cr} = \frac{1}{2} \arcsin \frac{2\tau}{\sigma_c} \quad (3)$$

σ_c composite tensile strength (assuming axially aligned fibers)

σ applied stress on composite

ϕ angle between fiber and tensile axis of specimen

τ shear strength of matrix or of interface

This equation differs from that presented in Refs. 4 and 7. For the model assumed in Ref. 6, $\sigma_c = \sigma$ rather than $\sigma_c = \sigma \cos^2 \phi$ for the different model of Refs. 4 and 7. The volume percent of fibers in a composite is constant with fi-

ber misalignment for the model of Ref. 6. The important thing to be concerned with here is that the fiber orientation in the discontinuous composites was extremely critical at elevated temperatures. It can be seen from the equation that by increasing the shear strength of the matrix (τ) the critical angle will be made larger and this will permit a greater safety factor in the incorporation of short length fibers in the matrix (i.e., the orientation does not have to be controlled so carefully). Another important point is that, since the strength of the composite (σ_c) would increase with increasing volume percent of the fibers, the critical angle would become less if the volume percent of the fibers were increased in a composite. For a discontinuous high volume percent fiber composite where the matrix would be weak when used at elevated temperatures, orientation of the discontinuous fibers would have to be very carefully controlled. To better appreciate the seriousness of the orientation problem, note the photograph of the shear failure specimen versus the tensile failure specimen shown in the figure 6.

Finally in considering creep-rupture or stress-rupture conditions, one might not anticipate that law-of-mixture relationships would apply. A program has recently been completed to better understand creep-failure or strengthening mechanisms of composites (8). As was the case for the tensile model system studies, the stress-rupture life and creep rates were based on several assumptions. For example: (1) the strains in the fiber and the matrix were assumed equal to each other in a composite and equal to that of the composite; (2) the fiber area fraction plus the matrix area fraction are equal to the area of the composite, which is taken as unity; (3) composite orientation is uniaxial, in a direction parallel to the axis of the specimen; and (4) that both constituents in the composite would fail by a tensile rather than shear mechanism. The components of the composites, again, are copper and tungsten which are insoluble in each other. Both creep-rupture and

stress-rupture behavior were studied to relate the properties of the composites to those of the components, fiber and matrix. The creep portion will be described first. If the equilibrium of forces in such a composite is considered, the stress distribution on the components could be expressed by the equation

$$\sigma_c = \sigma_f A_f + \sigma_m A_m \quad (4)$$

at a given creep rate $\dot{\epsilon}_i$

where

- σ stress on each component
- A relative area of each component
- $\dot{\epsilon}$ secondary creep rate
- c composite
- f fiber
- m matrix

From the above assumptions, a general equation shown in equation (5) was derived.

$$\sigma_c = \left[(\sigma_f)_o A_f + (\sigma_m)_o A_m \right] \dot{\epsilon}^\psi \quad (5)$$

where σ is stress on one component tested individually, and subscript o denotes the stress required to give a creep rate of 1 percent per hour, ψ is slope of log stress - log creep rate curve.

From this analysis, it was postulated that the creep rate of composites may be predicted by an exponential form of the law-of-mixtures equation. The experimental data obtained to verify the equations is given in figure 7. For constant creep rates, the composite strength increases as a straight line. By enlarging the lower parts of this curve as in figure 8, it can be shown that the lower portions of the curve extrapolate to stress values equivalent to those for the creep rates of the pure material comprising the matrix. For material such as those in the composites with widely diverging proper-

ties, the stresses for given creep rates of composites obey a law-of-mixture relationship. A similar relationship is true for stress for rupture versus volume percent fiber for given times of rupture life. Several equations with varying degrees of complexity were developed. A simplified equation from Ref. 8 permits the use of stress-rupture data for fiber and matrix materials to calculate the strength of the composite. In this case, the stresses for a given rupture time of the fiber and the matrix can be related by

$$(\sigma_c)_t = \left[(\sigma_f)_t A_f + (\sigma_m)_t A_m \right]_{t=\text{constant}} \quad (6)$$

The analysis of this equation would be similar to that presented previously for the calculation of the creep rate. A linear relation exists between composite stress and fiber content, with the stress on each component, for a given rupture time, as the end points of the straight line. Equation (6) can be expanded to a more general form similar to equation (5) (8). The qualifying assumptions to arrive at this type of equation for a stress-rupture situation were somewhat more numerous than those for the creep data. On the other hand stress-rupture data are far more readily obtainable than is creep data and far more easily used in designing practical composite materials. The main precautions, of course, are that many factors such as lack of compatibility between materials, lack of bonding, or other problems, might cause deviations from a law-of-mixtures type of prediction.

This brings us to consideration of compatibility problems which we have investigated to some degree with model systems. A complete lack of reaction between fiber and matrix, either during fabrication of the composite or during the service life of the composite would be desirable. However, since most practical materials react to some degree, techniques to minimize the effects of incompatibility are necessary. Variations of fabrication practice have been explored to minimize that portion of

composite incompatibility. Several fabrication methods have been used for composite materials; liquid state infiltration or solid state sintering of the matrix about the fibers are two examples. Powders may be consolidated about the fibers by various means such as slip casting and sintering, diffusion bonding, explosive deformation and many other methods. In any case, many methods of consolidation require a relatively high temperature to fabricate the composite. This subjects the fiber to a potentially degrading process. Initially, the effect of compatibility of materials on composite tensile strength has been studied at NASA by using copper base alloy matrix materials and tungsten fibers (9). Work was done using a liquid phase infiltration process. Aluminum, chromium, cobalt, columbium, nickel, titanium, and zirconium were added to the copper to determine their mode of reaction with tungsten fibers. They were added in percentages as high as possible which would permit the same temperature of infiltration to be used about tungsten fibers as was used in the case of pure copper, namely 2200° F for 1 hour in a vacuum atmosphere. Figure 9(a) shows photomicrographs of the cross sections of tungsten fibers in pure copper matrix. Note that there is no recrystallization or peripheral damage on the surfaces of the fibers. The tungsten fibers were damaged when nickel was added to the copper matrix. The damage is shown in figure 9(b) in the form of a recrystallized zone on the periphery of the fiber. Composites with fibers containing a zone like this were considerably weaker than those in which no recrystallization or penetration of the fiber occurred. As the penetration distance increased, the strength decreased rather drastically. It was postulated that the drastic decrease was due to an embrittling of the fibers by the recrystallized layer on the periphery. Once the brittle layer on each fiber was large enough to form a crack of a critical size, the crack could propagate through the notch-sensitized fiber and catastrophically damage the composite. Other types of reaction have been observed at peripheries of fibers and, in the matrices surrounding the

fiber. These also lowered the properties of the composites. Similarly other investigators have observed that brittle phases that form on the surface of a fiber such as intermetallic compounds, cause a similar degradation of the composite. It was found that brittle zones about the fibers are less degrading when the composites are utilized at temperatures above the ductile to brittle transition temperature of the fibers. If the degradation that occurs in fibers as a result of reaction is not catastrophic and can be tolerated, the situation is similar to that which occurs in a normal alloy in which losses of properties occur with time and temperature.

Another type of study recently completed is the study of interfiber distance and temperature on the critical aspect ratio in composites (10). Several mechanisms relating composite strength to increased matrix strength are given in the literature. Typical of these are work hardening, restraint of the matrix, and Poisson ratio effects (4, 11, and 12). We investigated the effects of interfiber distance on the strength of composites by studying the critical lengths or aspect ratios of fibers using pull-out tests (10). We utilized specimens such as that shown in figure 10. The specimen consisted of a button and fiber of one material and a matrix between the fiber and the button. The distance between the fiber and the button could be varied by varying the size of the hole drilled in the button. As shown in the figure, the thickness of the button controlled the shear length of the fiber-matrix interface and was designated L . With a button thickness (equivalent to shear length of the fiber-matrix interface) less than the critical length of the fiber, the fiber would pull out of the matrix in a tensile test. Whereas, with increased button thickness, when the critical length was equalled or exceeded, the wire fractured (see fig. 11). Tests to determine interfiber distance effects were conducted at room temperature using iron fiber-cadmium matrix and iron fiber-lead matrix composites. In addition, the effects of temperature on the critical aspect ratio for a constant in-

terfiber distance were determined using tungsten fibers in a copper matrix. Figure 12 shows a typical curve obtained for iron fiber-lead specimens. The failure load for a number of specimens is plotted against the aspect ratio. The failure mechanism changes from shear of the matrix to a tensile failure of the fiber at an aspect ratio of approximately 6 for a 1 mil interfiber distance. Curves such as those of figure 12 were used to obtain the critical aspect ratios resulting from variations of interfiber distances from 0.1 to 5 mils. A cross plot of critical aspect ratios versus interfiber distance is shown in figure 13. Data such as this can be used to calculate the shear strength of the matrix fiber interface as it relates to interfiber distance. Figure 14 shows a change in shear strength of the lead and cadmium matrix related to interfiber distance. The calculated shear strength of the lead was increased by 825 psi while the cadmium was increased by 900 psi when the IFD was decreased 5 mils to 0.1 mil. Thus for decreasing interfiber distances the shear strengths were increased.

The effect of increasing temperature on the critical aspect ratio of fibers is portrayed in figure 15 for the tungsten wire-copper specimens. It is evident that the critical aspect ratio increases very drastically as the temperature increases, which would be expected from the relative decrease in the shear strength of the matrix with respect to the strength of the relatively stable fiber material at the test temperatures used.

FIBER REINFORCED SUPERALLOYS

The concept that fiber reinforced composites could be tailored to do different jobs has been discussed for some time. In Ref. 13 a description of tailor making a composite was given for the utilization of high melting point fibers in a low melting point. Figure 16 shows a schematic illustration that aids in understanding how a high melting point fiber, such as a refractory metal or a ceramic, could operate at a fraction of its melting point in a

matrix superalloy. Little degradation of properties would occur if the fibers did not react with the matrix. Such materials would be expected to have unusually good high temperature strength. It was shown in model systems studies such as that of Ref. 8 that at 1500° F tungsten fibers in a copper matrix could have unusually good 100 hour stress-rupture strength in comparison with commercial superalloys such as Renee 41 and SM 200. One of the earliest available high strength tungsten wire was GE material 218 C.S. This was the material that was used for the bulk of our model systems studies. In the stress-rupture study of this material (14), it was found that this material had an exceedingly high strength in stress rupture at temperatures as high as 2500° F. A stress for 100 hour stress rupture life curve is plotted in figure 17 against test temperatures up to 2600° F. The tungsten wire is superior not only to superalloys by a considerable amount but also to other refractory metals some of which are exceedingly strong. Considering the left hand portion of the figure, it would be obvious that if these tungsten fibers were embedded in matrices of the superalloys indicated also in the figure, the composite that would result would have a strength in between that of the tungsten fiber and the matrix, assuming that the matrix did not catastrophically damage the fiber. The law-of-mixtures held for mutually insoluble copper and tungsten systems; however, reactions between fibers and metal matrix may occur in practical materials during fabrication and use, if the use temperature is high enough. Even thermodynamically stable materials such as highly refractory oxides may react with metallic matrices. Diffusion of metallic materials into the oxide as well as dissolution of the oxide in the matrix are possible. For high temperature material applications most material combinations of metal fiber and metal matrix have constituents which dissolve into each other. Composites with excellent properties are possible despite the dissolution or reaction with metal matrix materials. Control of

matrix-fiber incompatibility will be required to achieve this excellent potential.

One of the interests of the Lewis Research Center has been the production of material for possible advanced gas turbine applications. In particular, the turbine bucket and the nozzle vanes have been considered as important material problem areas and as such materials for these components are desired. Fiber reinforced superalloys would be a logical candidate for these components, particularly for the turbine bucket. Efforts have been undertaken to study fiber reinforced superalloys for potential use as air-breathing engine components at temperatures of 2000° F and above. Also, contracts have been awarded by the Lewis Research Center, to produce improved refractory metal alloy wires for use as reinforcement of superalloys.

Other investigators have produced composite materials with very high stress rupture strength. For example, the National Gas Turbine Establishment in Great Britain has produced fiber reinforced superalloys (15), some of which obey the law-of-mixtures relationships, and which have very good strength. Their method of fabrication was liquid infiltration about bundles of fibers. The Clevite Research Center (16) has also produced fiber reinforced superalloys by a powder metallurgy technique. In both cases relatively conventional superalloy compositions were used for the matrix materials. In the case of the Clevite work, for example, such alloys as Hasteloy X were powdered and used as a matrix. In both of these cases the volume percent of the fibers were no greater than 50 volume percent and in most cases the specimens had percentages ranging up to 30 volume percent. In work under way at the Lewis Research Center, an approach to produce high volume percent composites and to vary both the matrix composition and the fiber composition was utilized (17). Although some early compatibility studies were made (9), it was not known to what degree combinations of elements would damage or react with the fibers embedded in them. The matrix materials, nickel

and cobalt, two of the chief high temperature alloy matrices, were known to severely degrade the properties of the tungsten fibers embedded in them. On the other hand, chromium and other materials like zirconium and titanium, in small quantities, were felt to degrade the fiber materials only slightly. The matrix compositions were selected based on a potential for good compatibility relationships and on variations of ductility of the matrix materials. Table I shows the compositions of the alloys utilized. The most simple composition used, Alloy 1, contained only the solid solution elements chromium and tungsten in a nickel matrix. Alloy No. 5 was also largely a solid solution type alloy containing chromium, columbium, tungsten, molybdenum, and tantalum and no intermetallic compound precipitates. This type of composition is known to be very ductile and is generally the basis for some types of high temperature alloys. The two titanium and aluminum bearing modifications of the above alloys, Alloys 3 and 7, had low and high percentages of titanium and aluminum respectively. These alloys were expected to contain γ' and possibly η , both of which would increase matrix strength and reduce the reactivity of nickel. The fact that aluminum was added to each of these materials permitted the reduction of the chromium content of the materials to get some oxidation resistance. It was felt that this compositional range would give a clue as to some of the factors pertaining to the stability of the tungsten fibers in the matrix as well as to one Molybdenum fiber alloy. The wire materials that were used were: TZM (0.5 percent Ti, 0.08 percent Zr, 0.015 percent C, bal. Mo), NF (tungsten-1 percent thorium), 3D tungsten-3 percent rhenium), and 218 C.S. (commercial tungsten). In general, the experiment was to evaluate composite compatibility when matrix compositions, fabrication practices, wire size and wire compositions were varied. Some of the effects of these variables will be described. The first approach was to utilize 8 mil wire as a fiber reinforcement. These wires were first given compatibility-studies for time periods of 100 hours at a temperature of

2000° F in the various matrices. The composites were compacted by slip casting and fabricating them by sintering at 2000° F for 1 hour in dry hydrogen. This treatment also drove off the slip cast medium and presumably reduced some or most of the nickel and chromium oxide films present on the surfaces of the powder. Examples of some of the diffusion and recrystallization zones produced on the periphery of the fiber are shown in figure 18. The variation in reactivity of the four matrix materials with 218 C.S. wire is illustrated by the four outer photos. The complete reaction of TZM molybdenum fiber with all matrix compositions is typified by the center photo. The two solid solution matrix alloys, Alloys 1 and 5 (which did not contain Ti or Al) were more reactive with the fibers than were the matrices containing Ti and Al, namely Alloys 3 and 7. Alloy 3 was considered the most compatible matrix with the fibers. The compatibility was indicated by the depth of penetration measurements of the recrystallized-penetration zone. Relative to wire compositions, the materials 218 C.S., which is the relatively pure tungsten fiber with some doping and the 3 D wire which contained 3 percent rhenium were more compatible with the alloys than were the other wire materials investigated. As a result of the compatibility studies, the 218 C.S. wire and the 3 D wires were utilized in the initial stress-rupture studies. Some of the stress rupture results obtained with fibers embedded in the various matrices fabricated using the initial fabrication process are shown in figure 19. This figure shows the volume percent of fiber needed to produce a given time to rupture for a stress condition of 15,000 psi at 2000° F. Stress-rupture properties were related to compatibility. Because of the high percentage of reaction of the area of the 8 mil fibers, it was felt that several corrective treatments could be utilized to improve the properties of the composites. One of these was to modify the sintering procedure utilized in the fabrication of the composites. This was done by first sintering the materials at 1500° F for 1 hour in dry hydrogen rather than 2000° F, as

was done initially. Densification was accomplished in an isostatic hot pressing unit, again first utilizing 1500° F for 1 hour and then 2000° F for 1 hour under helium pressure of 20,000 psi. The second modification in the approach was made by the use of larger size fibers. Neglecting for a moment the aspect of changing the fabrication procedure and considering only the aspect of varying the diameters of the fibers; it should be evident that a large fiber with a given diffusion penetration type of damage would be damaged less than a small fiber. Thus, for example, an 8 mil wire with a 2 mil penetration zone would have 75 percent of the area of the fiber damaged to some degree by the reaction while the same penetration on a 20 mil fiber would only be 36 percent of the fiber that would be damaged. On the other hand, the larger diameter fibers usually are not as strong as the smaller diameter fibers in stress-rupture or in high temperature tensile values. Therefore, the two of these factors have to be balanced. Figure 20 shows a graphical method used to illustrate schematically how the composite strength varies with wire size and depth of the reaction for different material. The stress on a reacted fiber for a rupture life of 100 hours is plotted against the reaction depth of the fiber for varying wire diameter. The plot shows that for reaction depths less than approximately 1 mil, the 8 mil wire is stronger than the other wire sizes. At thicker reaction depth the larger diameter fibers are stronger. This is consistent with results obtained on composites containing various wire diameters. The best composite properties were obtained using 15 mil diameter wires and the modified fabrication technique. The properties obtained are shown in figures 21 and 22. Figure 21 shows the rupture strength versus test temperatures for 100 and 1000 hours of fiber reinforced composites containing 70 volume percent fibers with alloy 3 the most compatible matrix and with either the 218 C.S. or NF fibers as wires. The composites containing the high volume percent fibers have strengths for 100 and 1000 hours at 2000° F which are several times higher

than those properties for the best cast Ni alloys shown for comparison. This is true on a strength to weight ratio also. The properties of the composite are compared in figure 22 with those typical of the best cast nickel superalloys such as M22 or NASA-TRW VI A. The composites are over twice as strong in stress density for rupture in 1000 hours at 2000° F. Some of the conclusions reached in the investigation are believed to be equal or more important than the strength obtained. First it is evident that fibers without coatings can be utilized in a practical matrix to produce useful composites. In this investigation as much as 90 percent of the strength of fibers was utilized in a composite exposed to 100 hours at 2000° F in contact with a practical superalloy matrix. Secondly, the reactivity of the fiber and the matrix could be varied by varying the compositions of the alloying elements in either of the two constituents of the composite. In this case high W and Cr with titanium and aluminum additions to the superalloy matrix seemed to be beneficial. Depending on operating time wire diameters were found to be important. Small diameter wires with their superior strength may be superior to larger wires for short time high temperature operations or for lower temperature applications. Larger diameter wire was superior to smaller diameter wire for long time operations at high temperatures because the property degradation occurred by peripheral reaction with larger wire caused a lesser percentage of the gross wire cross section to be damaged. Finally, the fabrication practices used to consolidate and form the composites can cause a considerable variation in the properties of the materials. This latter information can be obtained in more detail from the original Ref. 17.

It was mentioned previously that contract work to produce higher strength refractory metal alloy fibers was undertaken under Lewis Research Center sponsorship. Some of these materials produced in the form of fibers had bulk material properties that were very interesting. The composition of the wires produced for the first series of studies

is indicated in figure 23 which shows 100 hour stress-rupture lives of the various refractory wires tested at 2000° and 2200° F (18). Another plot of the same data on a strength to weight ratio basis is given in figure 24. Many of the materials that were tested have adequate strength to weight ratios to reinforce a superalloy matrix. The highest strength to weight ratio material indicated is the tungsten with 2 percent ThO₂ dispersoids embedded in the matrix. If this material were embedded in a superalloy matrix, properties that are shown in the next figure 25 could be obtained. This figure shows 100 hour stress rupture strength and specific strength or strength to weight ratio for 100 hour rupture life. For comparison, properties typical of the best cast nickel base alloys, and TD-Ni, a dispersion strengthened material, are shown. The strength of the present 70 volume percent composite that was obtained (from Ref. 17) and the improved composite that could be obtained with the wires or fibers just described are also shown. New fiber materials are now under study. It is expected that some of these will have even higher strength to weight ratios than those shown previously.

WHISKERS

Whiskers have incited greater interest because of their unusually high strength and high temperature stability. It would be desirable to have very stable whiskers such as ceramics with very large length to diameter ratios (L/d) for reasons to be described subsequently. High strength whiskers with large L/d ratios are available in the form of wool or mats. The first problem associated with the use of these whiskers is the separation of discrete, useful, whiskers from the mat. The minimum L/d ratio desired for whiskers for high temperatures creep-rupture use is estimated to be on the order of 500/1 or more. This value of 500/1 is based on several assumptions, that the creep shear strength of the matrix and the creep-rupture strength of the whiskers are known or can be approximated from

known strengths. Further it must be assumed that a good bond between the fiber and the matrix exists so that pull out of the whiskers from the matrix would depend on the shear strength of the matrix. Actually, this is one of the main problems associated with embedding whiskers in a practical matrix, namely, that it tends not to bond well with the matrix. A poor bond would tend to increase the required length to diameter ratio to utilize the full whisker strength. Additionally, a large L/d ratio would be desirable to promote better orientation during the fabrication of the composite. The most commonly used technique to obtain usable whiskers from the mats is to separate them with the use of a blender. This normally produces whiskers that are of the order of 25/1 to 100/1 which are less than those desired for high temperature use. Most of the investigation done with the short length whiskers were bonding studies which can be done adequately with whiskers of less than the maximum optimum L/d ratios. Room temperature properties were obtained from most of these studies where short lengths are adequate to reinforce the matrix materials.

To appreciate the minute sizes and the difficulties associated with handling such fine particles, consider the fact that a 500/1 L/d whisker, with a 2 micron diameter, would be 0.04 inch long. Materials such as graphite fibers, which normally are approximately 8 microns in diameter, would be 0.16 inch long which is at least more visible. If you were to use a 4 mil diameter boron fiber chopped to 500/1, the fiber length would be 2 inches. We have obtained mats of alumina and silicon carbide whiskers and are beginning to investigate techniques for separating adequately sized whiskers from the mats.

POLYCRYSTALLINE CERAMICS

Stability at high temperature in a matrix is the primary reason for desiring ceramic fibers for high temperature composites. Polycrystalline ceramic fibers considerably larger than whiskers in diameter in spoolable lengths would

be most desirable. From a size standpoint alone larger diameter materials would be inherently stable relative to very fine products. Two types of stability that should be considered are one based on thermodynamic considerations and the other on resistance of the fibers to mechanical property degradation. Polycrystalline ceramics in fiber form have been shown to be superior in strength to bulk ceramics but not as strong as the nearly perfect single crystal whiskers. Some of the brittle materials such as boron, graphite, and alumina which have been made in fiber form have strengths in the range of 300,000 to 500,000 psi. These materials have been made in larger sizes than whiskers and in continuous lengths. No satisfactory process has been developed to produce refractory oxide materials which are of the greatest interest for fiber reinforced superalloy applications. Fibers that have been produced have not been of consistent quality for high temperature reinforcements. We are approaching this problem from two directions. The first is by attempting to elongate and extrude ceramics in metallic matrices to lengths adequate for fiber reinforcement. The second is to promote by contractual efforts the development of other methods to produce continuous polycrystalline ceramic fibers. Initially, our in-house effort consisted of elongating several oxide and ceramic powders in a matrix of tungsten. This work was published in reference 19. L/d ratios of as much as 29/1 were obtained for the oxide ZrO_2 and 18/1 for hafnium nitride. Later a series of widely different types of oxides were embedded in matrices of columbium and tantalum and extruded at different ratios and different temperatures (20). L/d ratios of as much as 19/1 was obtained for ZrO_2 in Cb. In the latest paper UO_2 was elongated in a tungsten matrix and an L/d ratio equivalent of 150/1 was obtained (21). In all of the preliminary studies strengthening increases which were obtained for the composites relative to the pure metals could not be proved to result solely from fiber reinforcement by the elongated ceramics. The importance of these

studies was that the feasibility of elongating these highly refractory oxides was demonstrated. Several factors associated with the elongation of these types of materials were noted. First, it was determined that higher temperatures were needed to soften the ceramic materials, but matrix stiffness was also needed. It was felt that the elongation process involved a shearing of the ceramic in the matrix of the material. This suggested that a high shear strength matrix (at high temperature) was desirable. It was also felt that larger particles would elongate to a greater degree than finer particles. To evaluate these concepts, some manipulations of the extrusion process have permitted us to produce fibers such as those shown in figure 26. Several fibers were over 1 inch long. As soon as possible we intend to obtain room and elevated temperature strengths of these materials.

Our most recent contract work has been to exploit the methods developed and to attempt to extrude several ceramic materials by a multiple extrusion process. This work is being conducted by the Whittaker Corp. with a goal of elongating the ceramics and removing them from the matrix for subsequent use. Other methods are being explored to produce refractory oxide fibers. The first contract which was initiated 3 years ago involved the expulsion of a liquid oxide through a small diameter orifice. The main problem associated with this method was the tendency for the jet of liquid oxide to break up into droplets rather than to remain in fiber form. The second problem was associated with the production of porosity in the fiber rather than a solid dense product. Fibers several inches long, of the order of 7 mils diameter, were produced by the process. Thus this method was demonstrated for production of fibers. Properties, however, were extremely low. It is intended to continue work of this nature on a contractual basis to develop longer fibers with improved properties by the same type of method. Other promising methods are being sought also.

FUTURE EFFORTS

While we are continuing to conduct model system studies to further develop our understanding of the behavior of composite materials, it is felt that sufficient information has been generated to warrant the development of materials with engineering properties. It is evident from some of the preliminary work that it is feasible to produce refractory metal reinforced fiber composites of very high strength at elevated temperatures. The higher the fiber strength, the stronger should be the composite. To this end we are continuing our contractual efforts to produce stronger fibers of such materials as tungsten alloys, dispersion strengthened materials, tantalum alloys, and columbium alloys. We are also continuing our effort to produce stronger ceramic types of fibers. This will include a continuation of our co-reduction method for producing ceramics and the solicitation and support of programs to develop polycrystalline ceramic fibers by novel means. Finally, diffusion barriers are of interest to minimize reactivity between the fiber and the matrix.

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TABLE I. - SELECTED NICKEL ALLOY MATRIX MATERIALS

[Nominal composition of alloy (wt. %).]

Alloy No.	Al	Cb	Cr	Mo	Ni	Ti	W	Ta
1	---	----	20	--	55	---	25	----
3	2	----	15	--	56	2	25	----
5	---	1.25	19	4	70.5	---	4	1.25
7	4.2	1.25	15	4	66.8	3.5	4	1.25

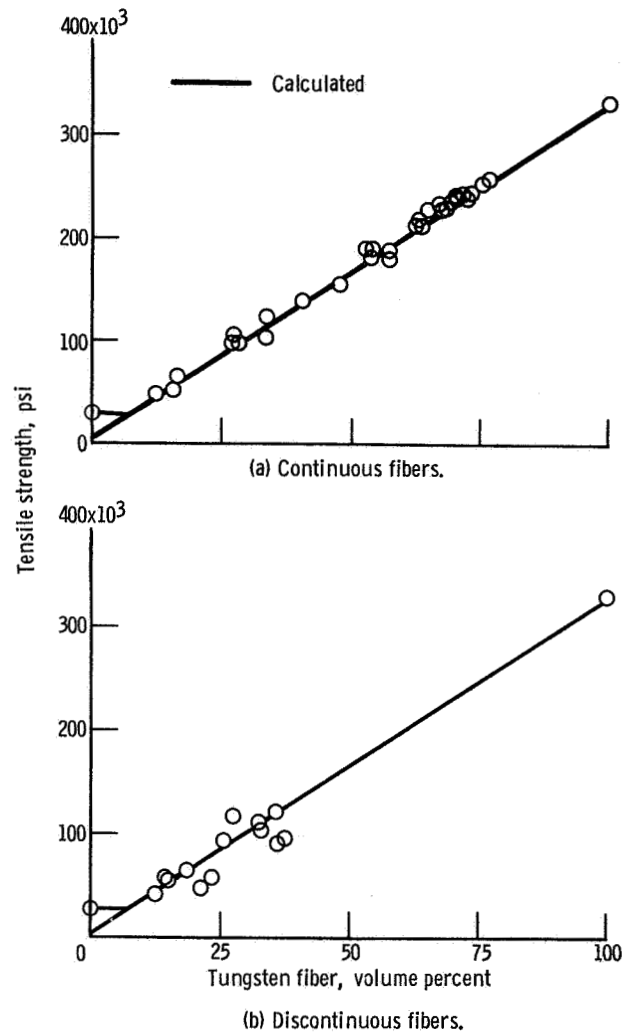


Figure 1. - Ultimate tensile strengths of tungsten-fiber-reinforced copper composites. Diameter of tungsten fibers, 5 mils (ref. 3).

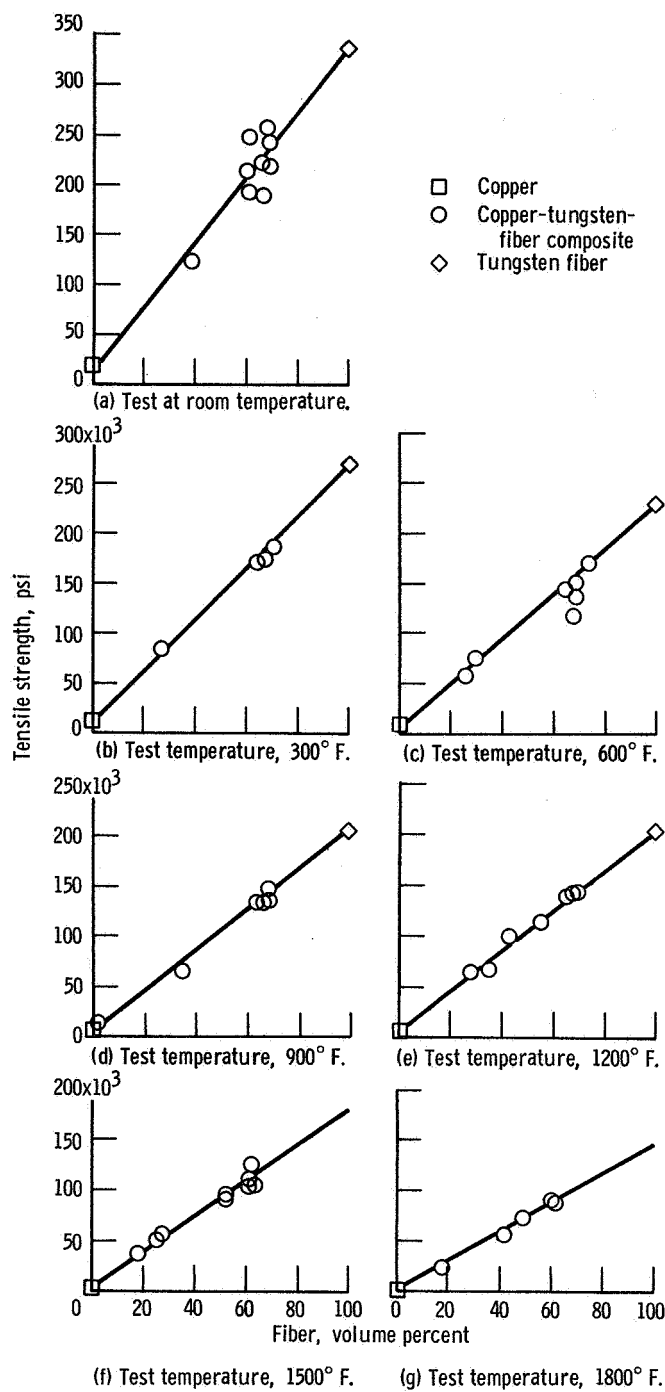


Figure 2. - Tensile-strength - composition diagrams for tungsten-fiber-reinforced copper composites as function of temperature. Continuous tungsten fibers (ref. 5).

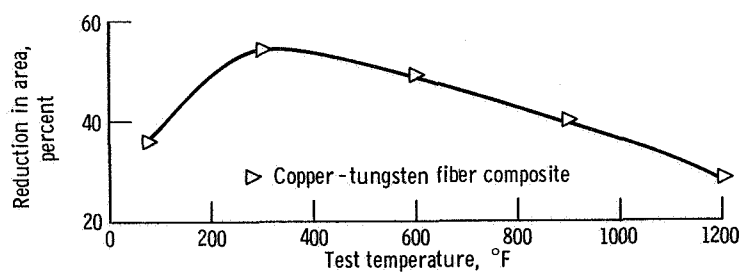
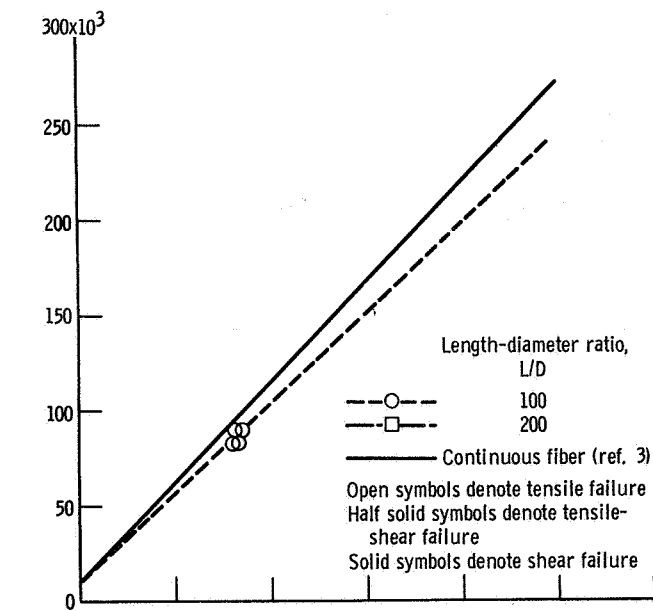
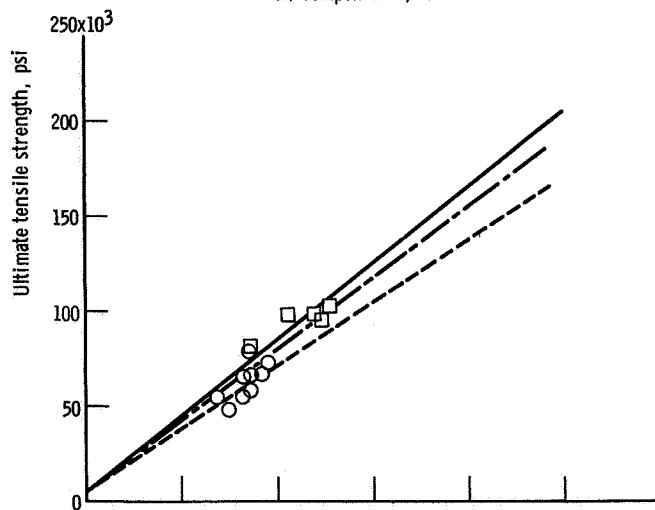


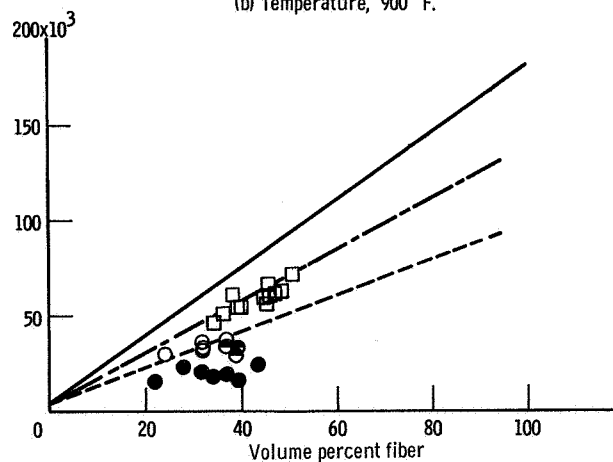
Figure 3. - Average percent reduction in area against test temperature for copper - tungsten fiber reinforced composites. Tungsten fiber, 70 volume percent (ref. 5).



(a) Temperature, 300° F.



(b) Temperature, 900° F.



(c) Temperature, 1500° F.

Figure 4. - Tensile strength as function of fiber content for discontinuous-tungsten-fiber-reinforced copper composites (ref. 6).

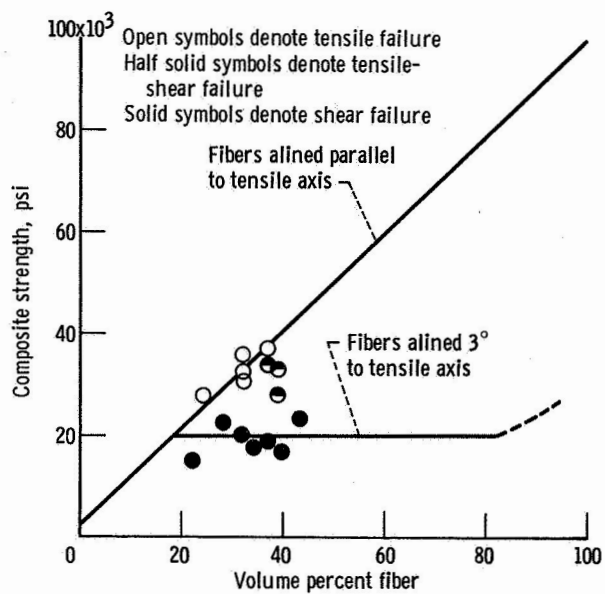
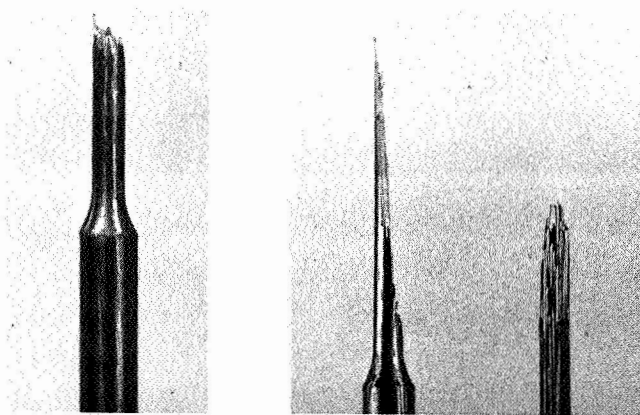


Figure 5. - Composite strength as function of fiber content and orientation for tungsten-fiber - copper-matrix composites with length-diameter ratio of 100 at 1500° F (ref. 6).



(a) Tensile failure.

(b) Shear failure.

Fig. 6. - Typical examples of test specimens that failed in tension or shear (ref. 6).

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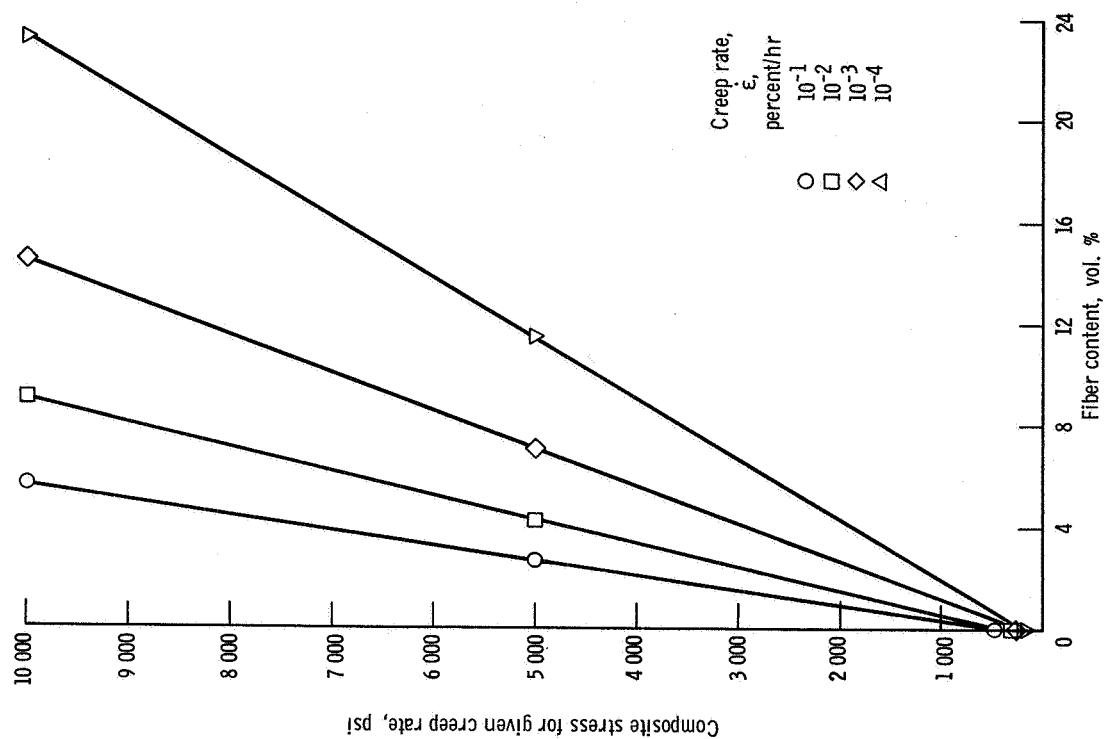


Figure 8. - Enlargement of low-fiber-content region of curve of stress for given creep rate - fiber content (ref. 8).

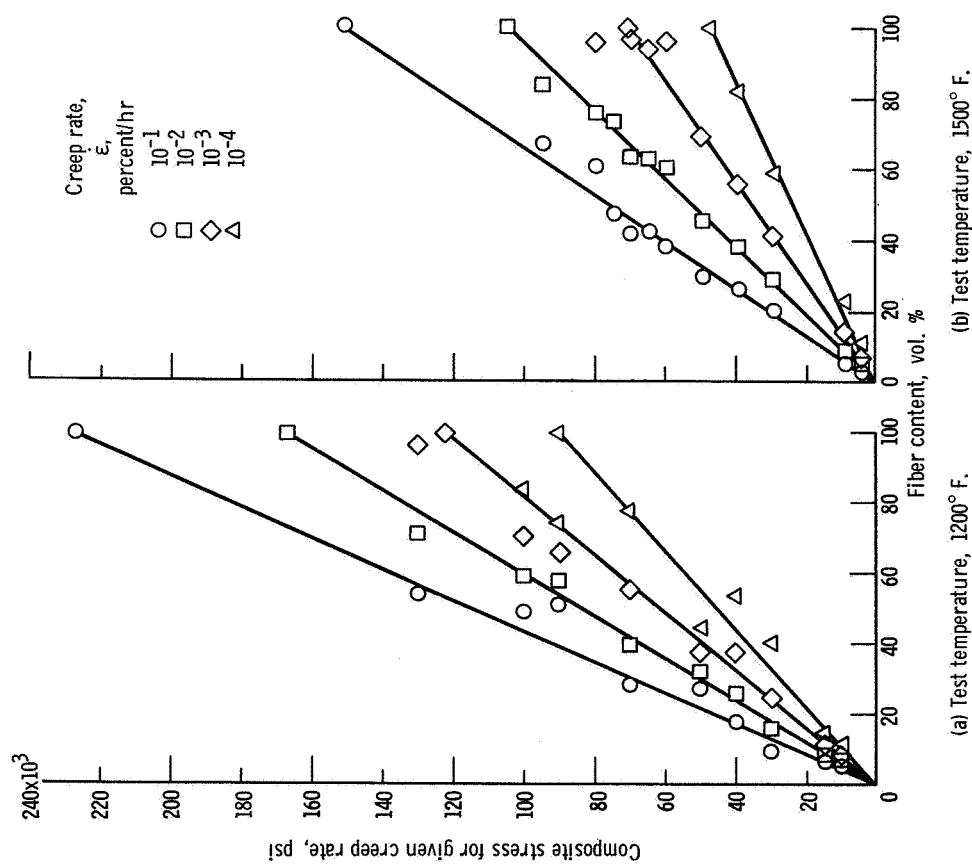


Figure 7. - Stress for given creep rate as function of fiber content for tungsten-fiber-reinforced composites (ref. 8).

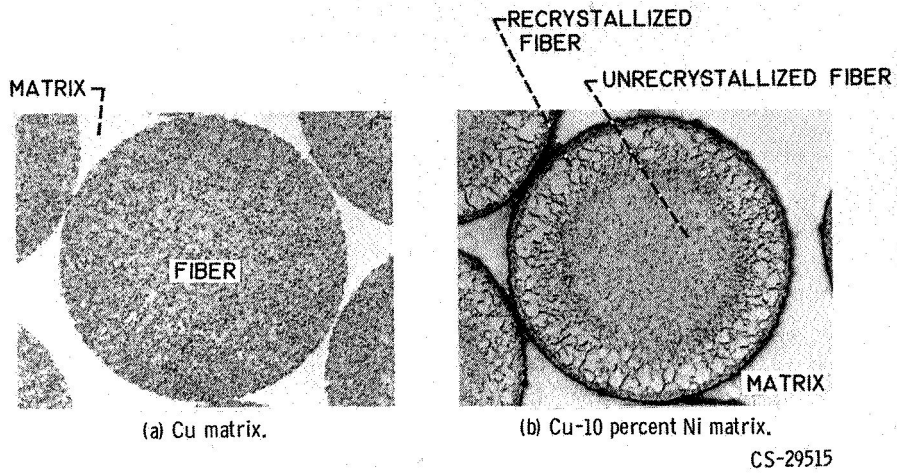


Fig. 9. - Tungsten fibers in copper alloy matrix; transverse section, as-infiltrated.

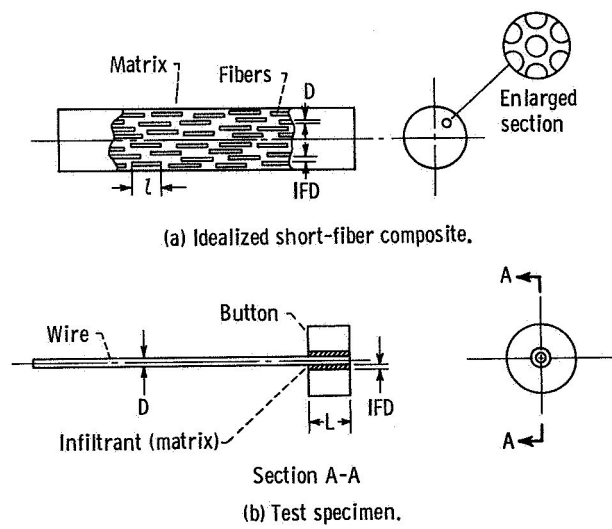
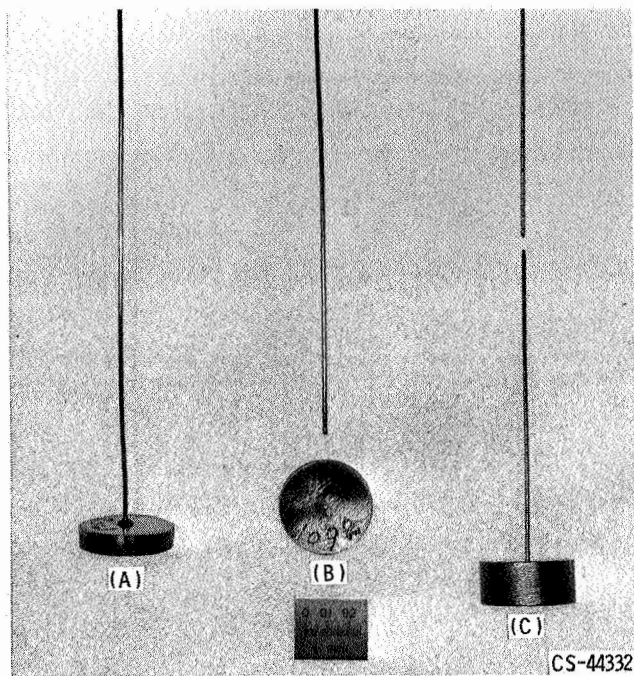


Figure 10. - Comparison of test specimen and short fiber composite (ref. 10).



(a) Before testing. (b) Pullout failure. (c) Wire failure.

Fig. 11. - Aspect ratio test specimens.

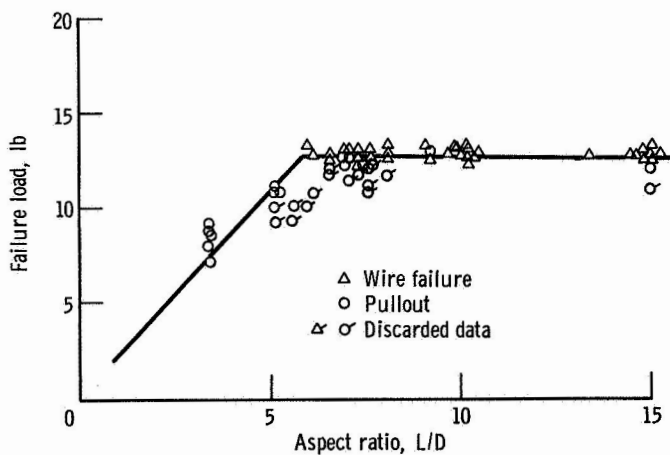


Figure 12. - Failure load and mode at various aspect ratios. Ingot iron-lead, room temperature; interfiber distance, 1.0 mil (ref. 10).

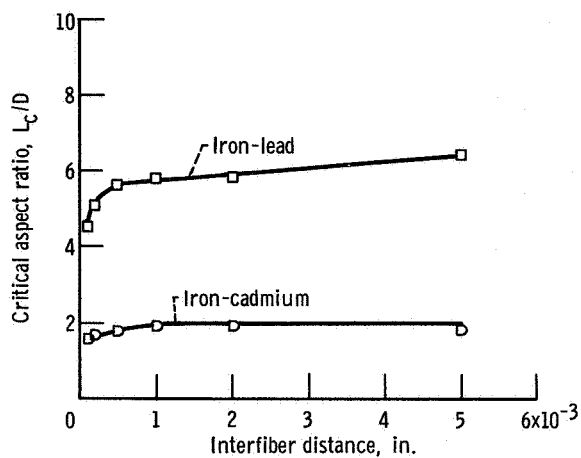


Figure 13. - Observed critical aspect ratio at various interfiber distances (ref. 10).

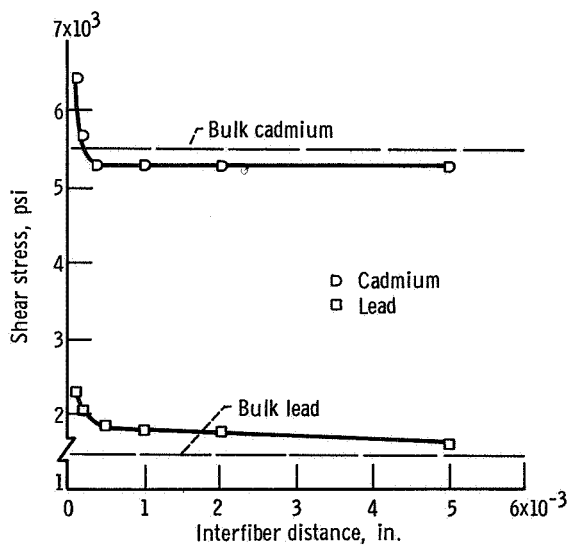


Figure 14. - Shear stress on infiltrant at various interfiber distances (ref. 10).

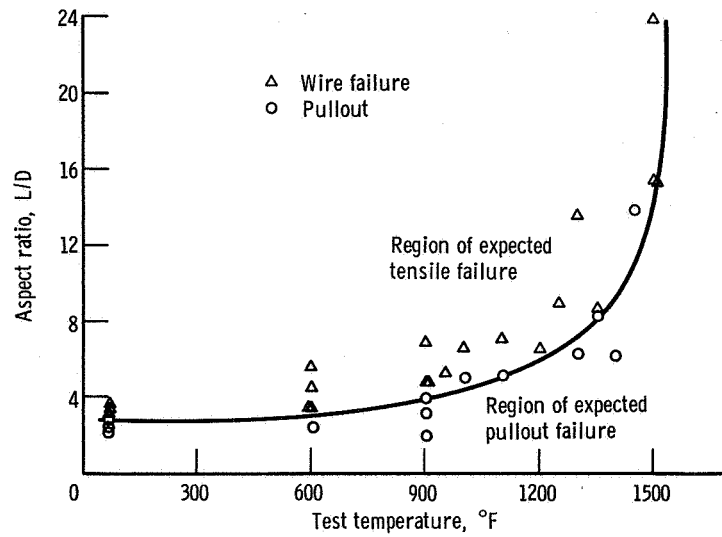


Figure 15. - Critical aspect ratio as a function of temperature. Tungsten wire-copper; interfiber distance, 1.6 mil (ref. 10).

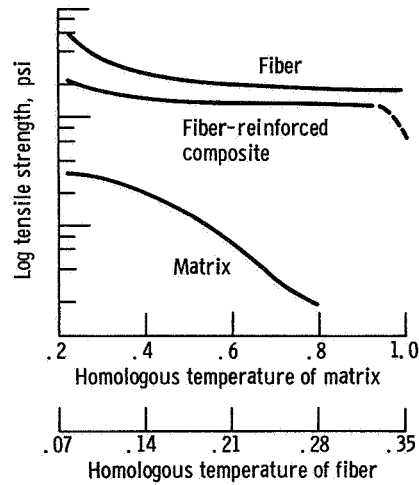


Figure 16. - Schematic comparison of tensile strength of composite and composite components as function of homologous temperature (ref. 13).

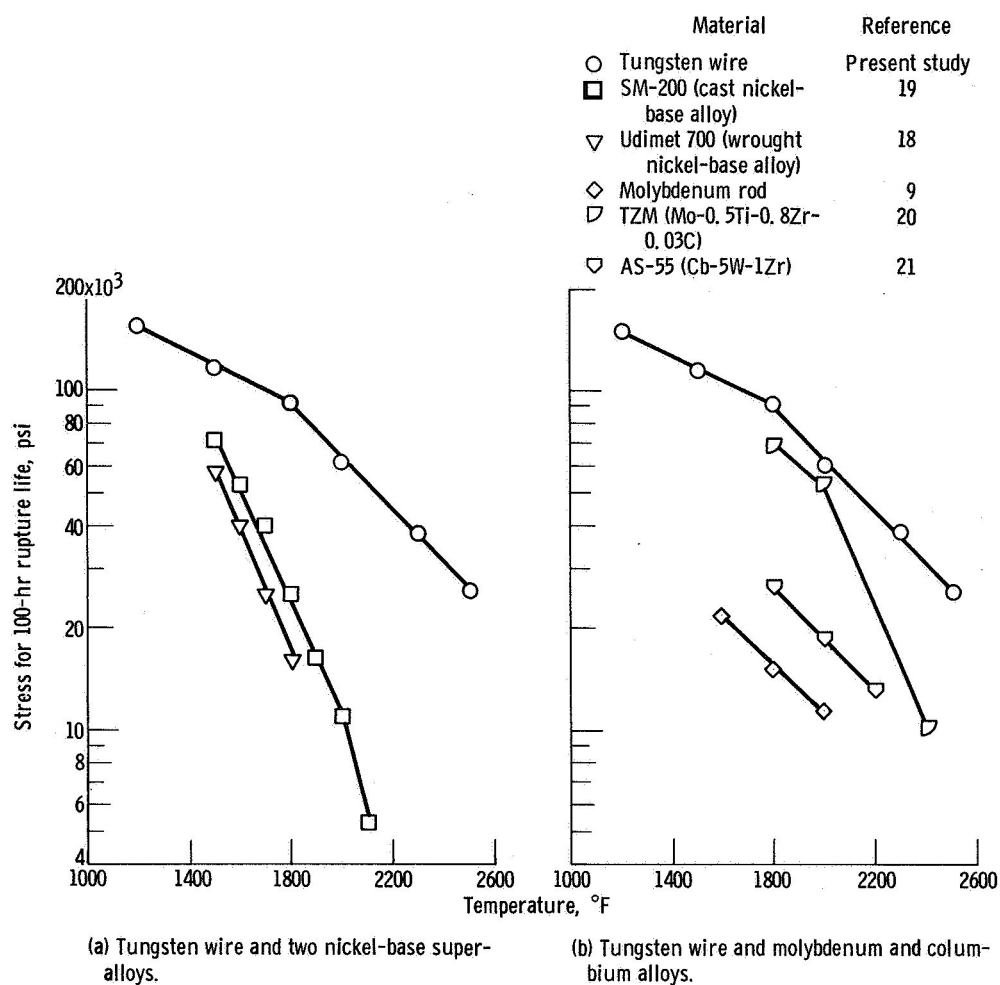


Figure 17. - Stress required for rupture in 100 hours as function of temperature (ref. 14).

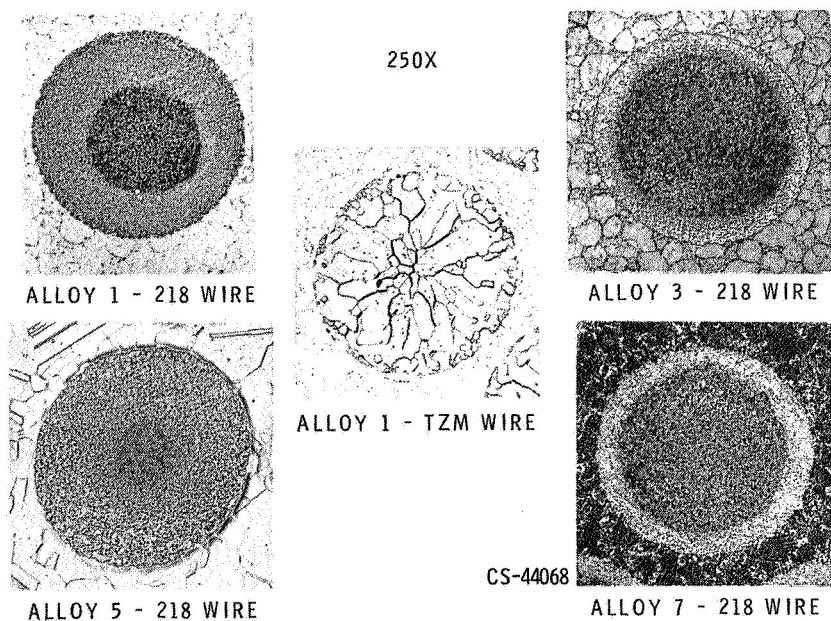


Fig. 18. - Microstructures of matrix-fiber reaction in as-fabricated composites.

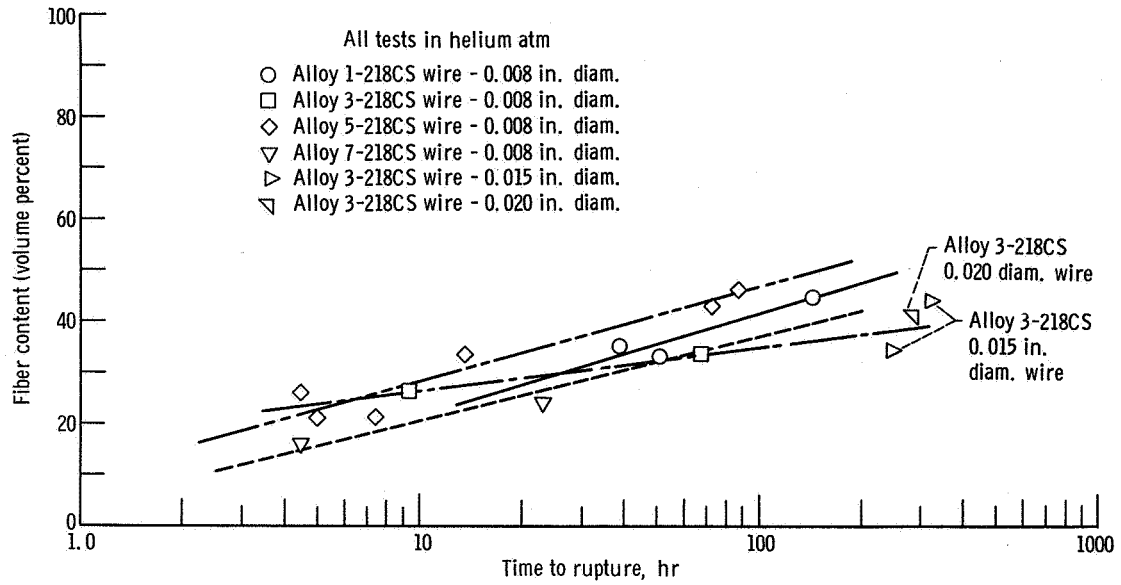


Figure 19. - Rupture properties of high temperature fabricated composites at 15,000 psi and 2000° F (ref. 17).

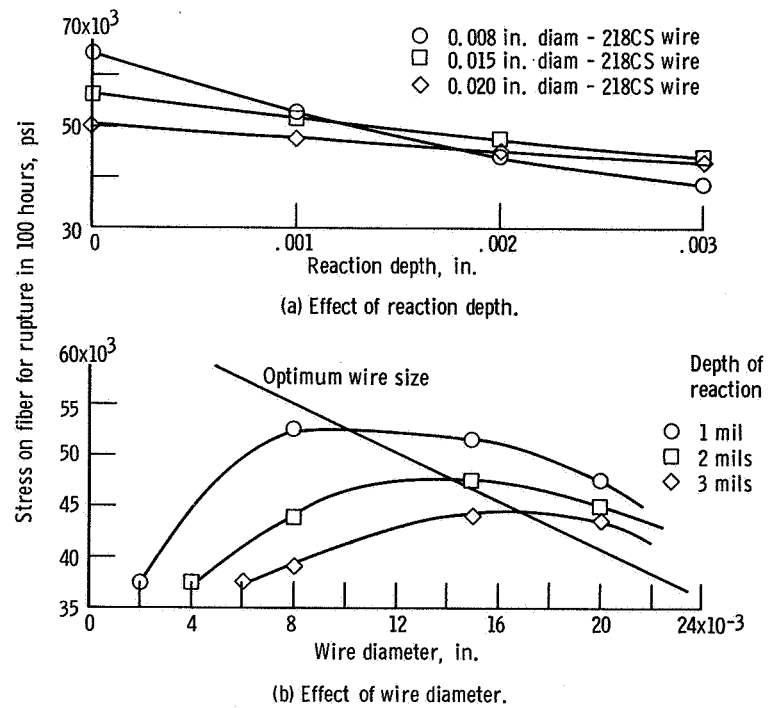


Figure 20. - Calculated 100 hour rupture strength of wire at 2000° F as a function of wire diameter and depth of penetration (ref. 17).

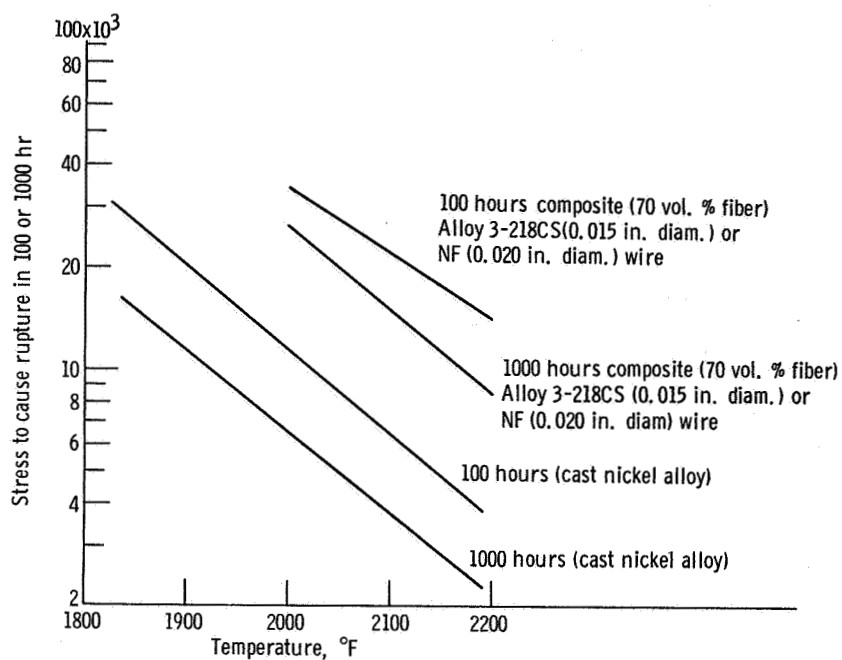


Figure 21. - Stress for rupture in 100 and 1000 hours of 70 volume percent composites and nickel alloy (ref. 17).

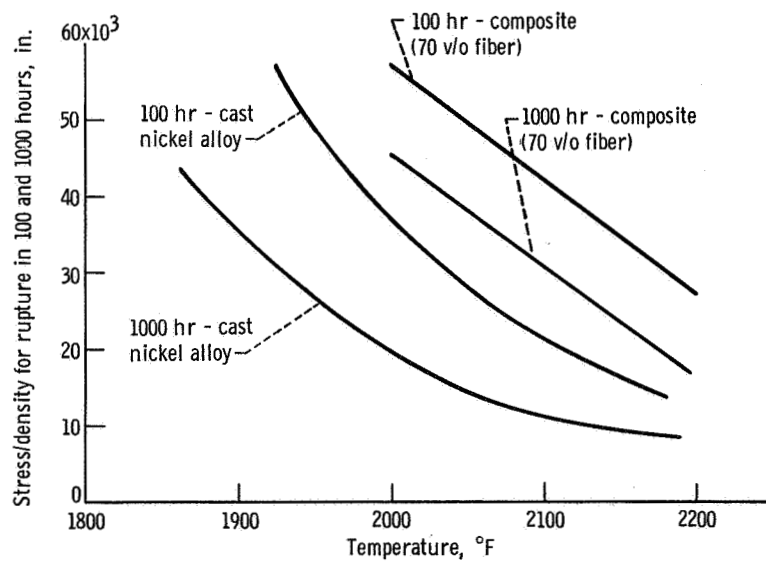


Figure 22. - Specific strength for rupture of composite and cast nickel alloy against temperature (ref. 17).

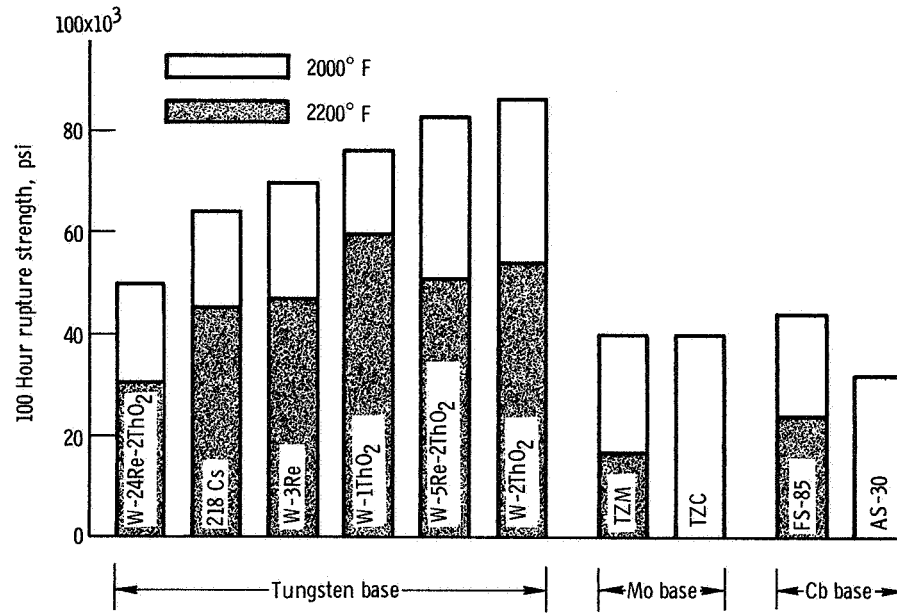


Figure 23. - 100 Hour rupture of refractory wire, 2000° and 2200° F.

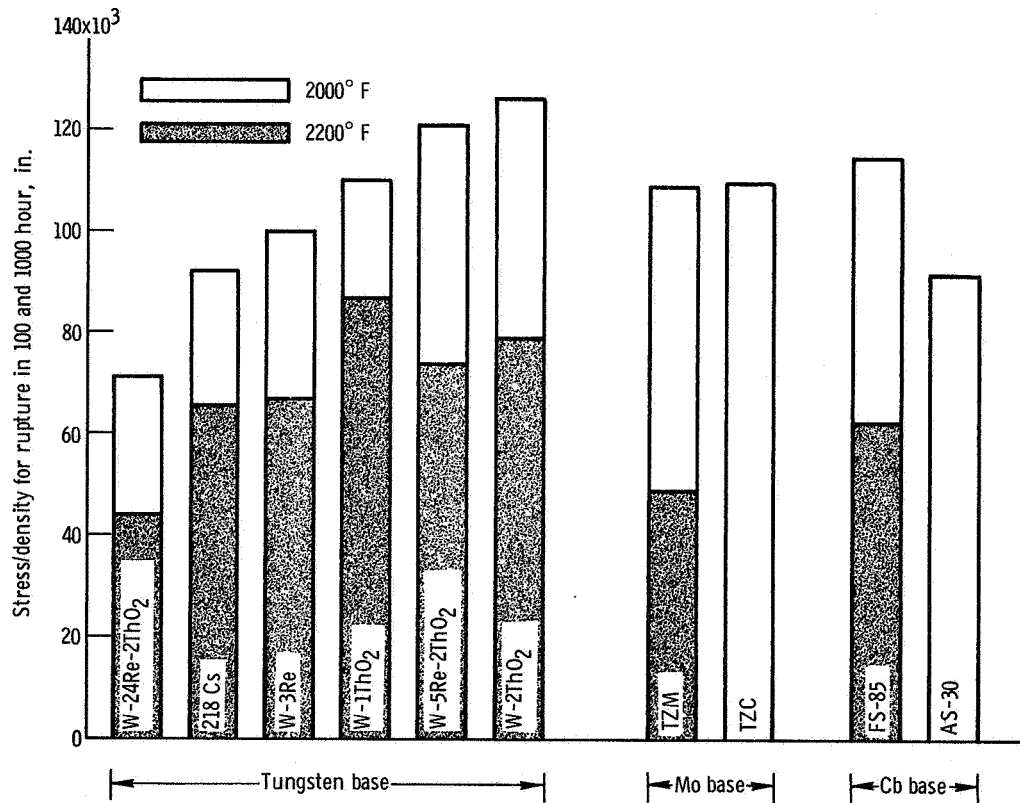


Figure 24. - Specific 100 hour rupture strength for refractory wire, 2000° and 2200° F.

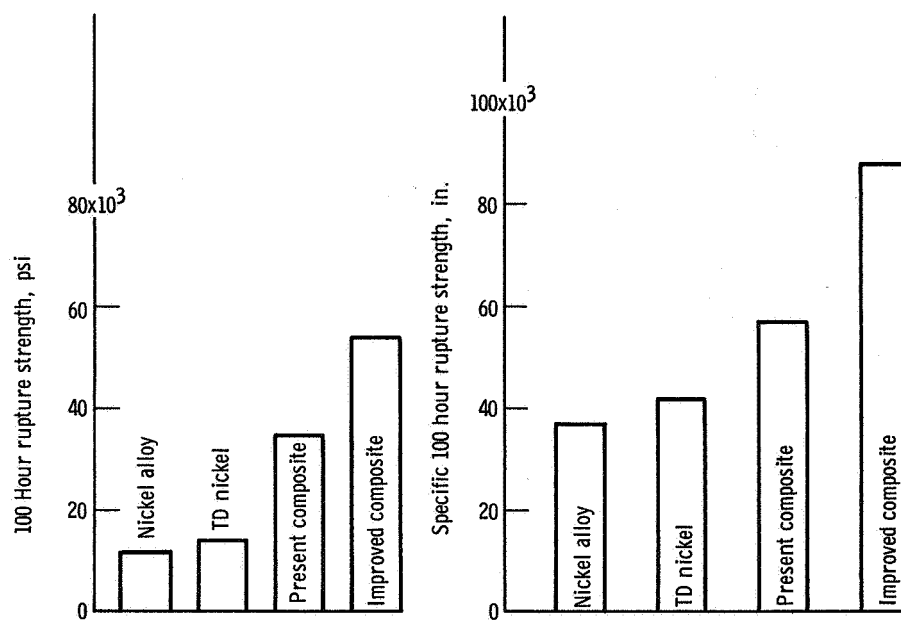
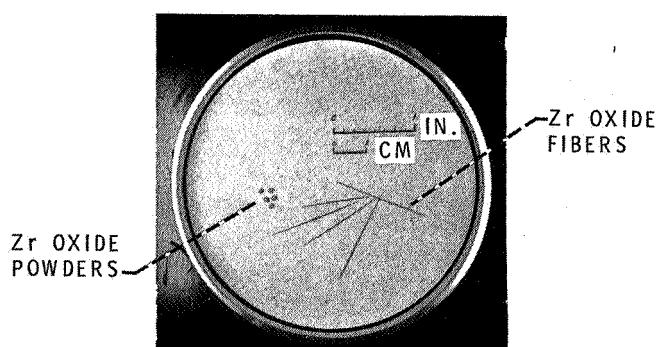


Figure 25. - Potential rupture strength, 2000° F.



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Fig. 26. - Zirconium oxide fibers produced by extrusion of powders within refractory metals.